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(54) Title: THE USE OF FLUORESCENT WHITENING AGENTS

(57) Abstract: The use of a polymeric carrier material treated with a fluorescent whitening agent, for lightening human skin and for protecting human skin against UV radiation, is described.

The use of fluorescent whitening agents

The present invention relates to the use of a polymeric carrier material treated with a fluorescent whitening agent, for lightening human skin and for protecting human skin against UV radiation.

Melanin is a dark pigment that is found in the hair, the eyes and, especially, the skin, and that is formed in the so-called melanocytes by the conversion of the amino acid tyrosine in the presence of the enzyme tyrosinase. The number of melanocytes varies widely according to individual skin type.

Frequently, local areas of skin are to be found that have an increased melanin density. In such areas the number of melanocytes is significantly elevated, resulting in a skin colour that is far darker than the colour of the rest of the skin. Such local, hyperpigmented areas are known as brown spots, age spots or liver spots.

Women who have borne children and/or have taken the contraceptive pill for a prolonged period are frequently more especially subject to such spot formation. This undesired colour change is considered in particular by many women to be a disfigurement, and frequently leads to serious emotional disorders. Also, in many cultures in which parts of the population are coloured, especially in the Asiatic region, a naturally dark skin type that has elevated melanin concentration is undesirable. In regions such as those, depigmentation compositions are preferably used to lighten the skin.

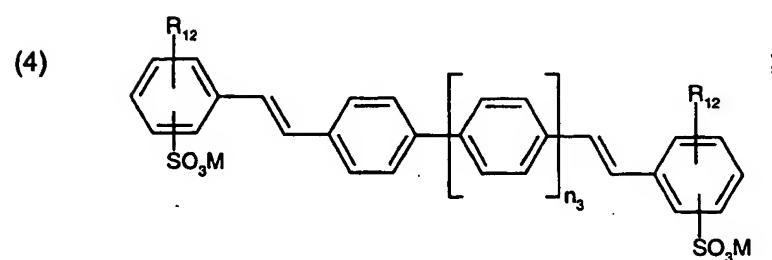
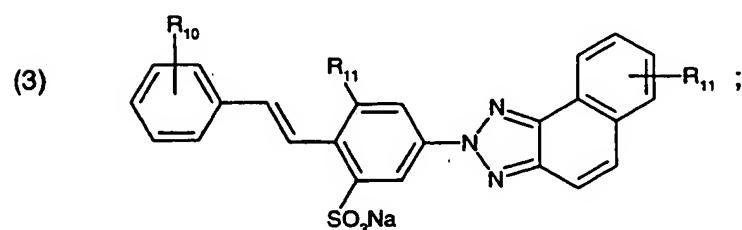
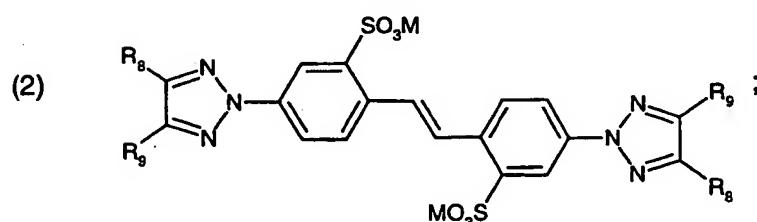
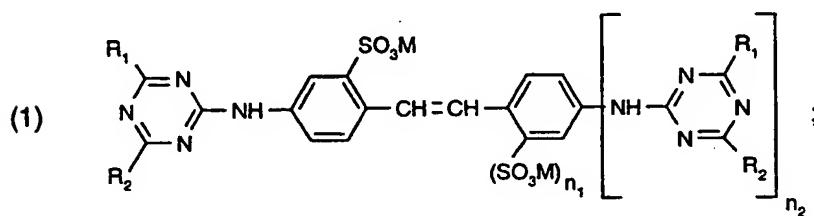
In the past a number of topical preparations have been proposed for the prevention of hyperpigmentation that comprise one or more components, so-called depigmentation agents or bleaching agents, e.g. hydroquinone, hydroquinone derivatives, hydrocortisone and retinic acid, benzoyloxyphenol (US-A-3 060 097) or methoxyphenol. Such components bring about depigmentation by the oxidation or reduction of melanin, but a disadvantage of those active ingredients is that they may cause undesired skin reactions, or satisfactory formulation thereof into cosmetic preparations is not possible.

The problem of the present invention is to make available skin-lightening compositions that on the one hand have the effect of lightening the skin and that on the other hand are well tolerated by the skin and can be formulated cosmetically.

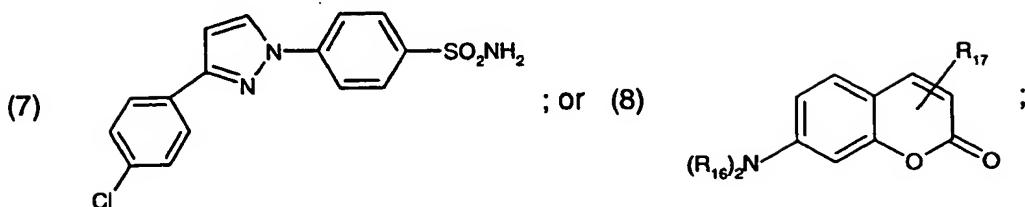
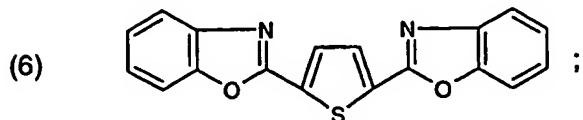
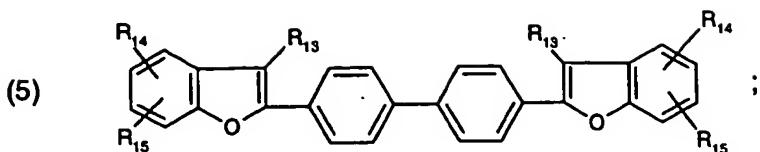
Surprisingly, it has now been found that a polymeric carrier material treated with a fluorescent whitening agent meets those requirements. In addition, such a material protects the human skin from the damaging effect of UV rays.

The present invention accordingly relates to the use of a polymeric carrier material treated with a fluorescent whitening agent for lightening human skin and for protecting human skin against UV radiation.

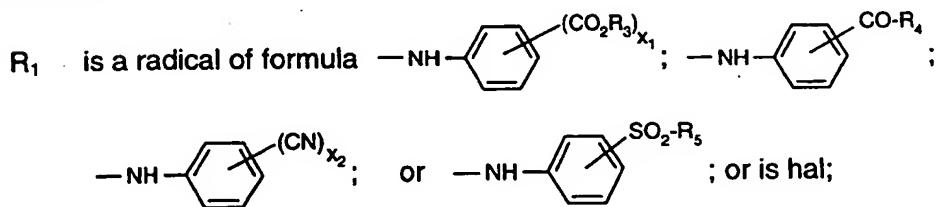
Preferred fluorescent whitening agents that can be used in accordance with the invention correspond to the formula



- 3 -



wherein

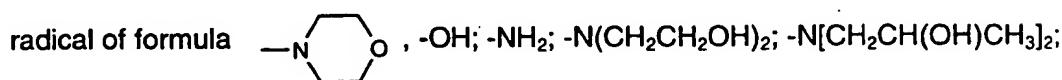


R_3 is M; unsubstituted or substituted alkyl or unsubstituted or substituted aryl;

R_4 is hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or $-\text{NR}_6\text{R}_7$, wherein R_6 and R_7 are each independently of the other hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or R_6 and R_7 together with the nitrogen atom binding them form a heterocyclic radical, especially a morpholino or piperidino radical,

R_5 is hydrogen, unsubstituted or substituted alkyl or unsubstituted or substituted aryl, or a radical of formula (1a) $-(\text{CH}_2)_{x_2}-\text{O}-\text{SO}_3-\text{M}$;

R_2 is hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or a radical of formula

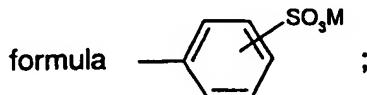


$-\text{NH}-\text{R}_3$; $-\text{N}(\text{R}_3)_2$ or $-\text{OR}_3$; or

R_1 and R_2 are each independently of the other $-\text{OH}$, $-\text{Cl}$; $-\text{NH}_2$, $-\text{O}-\text{C}_1\text{-C}_4\text{alkyl}$, $-\text{O}-\text{aryl}$,

-NH-C₁-C₄alkyl, -N(C₁-C₄alkyl)₂, -N(C₁-C₄alkyl)(hydroxy-C₁-C₄alkyl), -N(hydroxy-C₁-C₄alkyl)₂; -NH-aryl, morpholino; or S-C₁-C₄alkyl(aryl);

R₈ and R₉ are each independently of the other hydrogen, C₁-C₄alkyl, phenyl or a radical of



R₁₀ is hydrogen, Cl or SO₃M;

R₁₁ is -CN, -SO₃M, -S(C₁-C₄alkyl)₂ or S(aryl)₂;

R₁₂ is hydrogen, -SO₃M, -O-C₁-C₄alkyl, -CN, -Cl, -COO-C₁-C₄alkyl or CON(C₁-C₄alkyl)₂;

R₁₃ is hydrogen; -C₁-C₄alkyl, -Cl or -SO₃M;

R₁₄ and R₁₅ are each independently of the other hydrogen, C₁-C₄alkyl, -SO₃M, -Cl or -O-C₁-C₄alkyl;

R₁₆ is hydrogen or C₁-C₄alkyl;

R₁₇ is hydrogen, C₁-C₄alkyl, -CN, -Cl, -COO-C₁-C₄alkyl, -CON(C₁-C₄alkyl)₂, aryl or -O-aryl;

M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C₁-C₄alkylammonium, mono-, di- or tri-C₁-C₄hydroxyalkylammonium, or ammonium di- or tri-substituted by a mixture of C₁-C₄alkyl and C₁-C₄hydroxyalkyl groups;

n₁, n₂ and n₃ are each independently of the others 0 or 1;

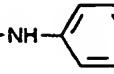
x₁ is 1 or 2; and

x₂ is from 1 to 3.

R₂, R₃, R₄, R₅, R₆ and R₇ in the meaning of (unsubstituted or) substituted alkyl is C₁-C₁₂alkyl, preferably C₁-C₄alkyl. The alkyl groups may be branched or unbranched and may be unsubstituted or substituted by halogen, e.g. fluorine, chlorine or bromine, by C₁-C₄alkoxy, e.g. methoxy or ethoxy, by phenyl or carboxyl, by C₁-C₄alkoxycarbonyl, e.g. acetyl, by mono- or di-C₁-C₄alkylamino or by -SO₃M.

R₂, R₃, R₄, R₅, R₆ and R₇ in the meaning of (unsubstituted or) substituted aryl is preferably a phenyl or naphthyl group that may be unsubstituted or substituted by C₁-C₄alkyl, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl, by C₁-C₄alkoxy, e.g. methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy, by halogen, e.g. fluorine, chlorine or bromine, by C₂-C₅alkanoylamino, e.g. acetylarnino, propionylarnino or butyrylarnino, by nitro, by sulfo or by di-C₁-C₄alkylated amino.

The compounds of formula (1) are preferably used in neutral form, that is to say M is preferably a cation of an alkali metal, especially sodium, or an amine.

In the compounds of formula (1), R₁ is preferably a radical of formula —NH——CO₂—R₃,

wherein R₃ has the meanings given above and is preferably C₁-C₄alkyl, especially methyl or ethyl; or a radical of formula —NH——CO—R₄, wherein R₄ has the meanings given above

and is preferably C₁-C₄alkyl, especially methyl or ethyl, or —NR₆R₇, wherein R₆ and R₇ have the meanings given above and are preferably hydrogen, C₁-C₄alkyl, especially methyl or ethyl, a morpholino or piperidino radical, more especially hydrogen, or a radical of formula

—NH——SO₂—R₅, wherein R₅ has the meanings given above and is preferably

C₁-C₄alkyl substituted by —SO₃M, especially methyl or ethyl substituted by —SO₃M, wherein M has the meanings given above and is preferably sodium; and

R₂ is preferably —N—O, —NH₂, —N(CH₂CH₂OH)₂ or —N[CH₂CH(OH)CH₃]₂.

The compounds of formula (1) can be prepared under known reaction conditions by the reaction of cyanuric chloride with the corresponding aminostilbenesulfonic acids and with an amino compound that is capable of introducing a group R₁ and with a compound that is capable of introducing a group R₂, R₁ and R₂ having the meanings given above.

The fluorescent whitening agents that can be used with advantage in the present invention are listed by way of example in the following Table 1:

Table 1:

<u>Compound of formula</u>	
(9)	
(10)	
(11)	

Table 1:

<u>Compound of formula</u>	
(12)	
(13)	
(14)	

Table 1:

<u>Compound of formula</u>	
(15)	
(16)	
(17)	

Table 1:

<u>Compound of formula</u>	
(18)	
(19)	
(20)	
(21)	
(22)	

Table 1:

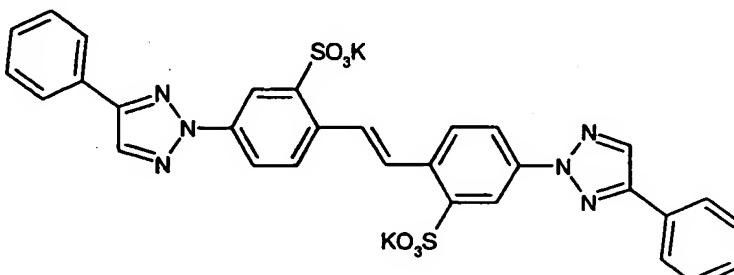
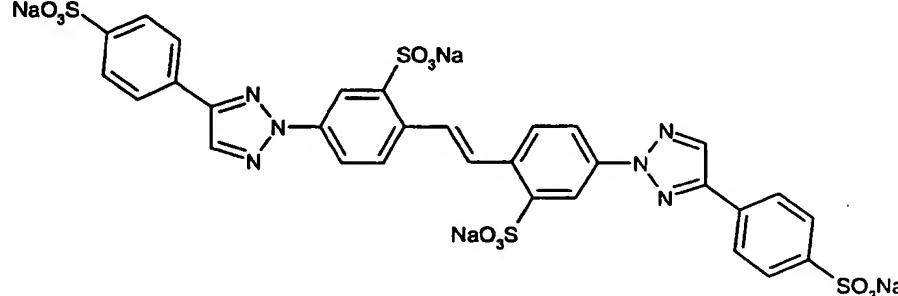
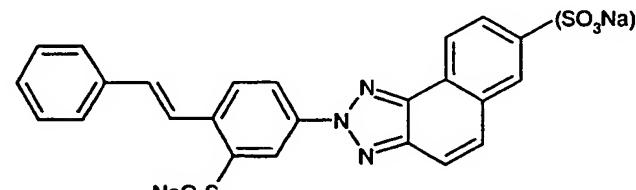
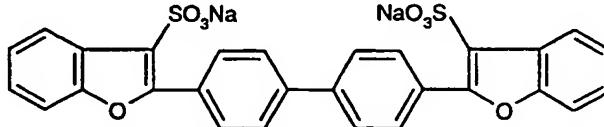
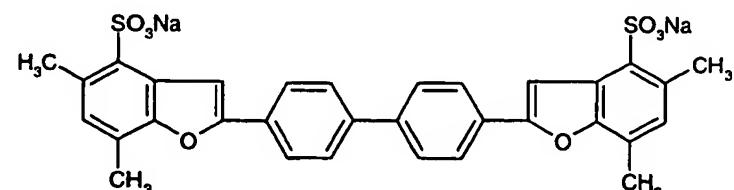
<u>Compound of formula</u>	
(23)	
(24)	
(25)	
(26)	
(27)	

Table 1:

<u>Compound of formula</u>	
(28)	
(29)	
(30)	

In principle, as polymeric carriers for use in accordance with the invention there come into consideration materials that are suitable for cosmetic or pharmaceutical preparations. The polymeric materials may be of natural origin or are obtainable synthetically, e.g. starch, starch derivatives, e.g. hydroxypropyl-distarch phosphate, polyvinylpyrrolidones, polyvinyl-polypyrrrolidones, polyacrylates, acrylates/steareth-20, methacrylate copolymers, acrylate copolymers, acrylate-octylpropenamide copolymer (Dermacryl 79), acrylate/vinyl isodecanoate cross polymer, C₁-C₁₀polycarbamyl-polyglycol esters; C₁-C₁₈polycarbamyl-polyglycol esters, acrylate/hydroxy ester acrylate copolymer, acrylate-octylacrylamide; polyacrylamide; polyamides, polyvinylcaprolactam, polyvinyl alcohols, polyolefin dispersions, polyesters, sodium polystyrenesulfonates, latex particles (of all kinds of polymers and copolymers), chitosan and derivatives, xanthans, Gellan, hyaluronic acid, cellulose, cellulose ethers, polyglucans, CM-glucans, alginates, hydroxyethyl cellulose, hydroxypropyl cellulose, cyclodextrins (α -, β -, γ -) and their derivatives, polyoxyethylene-polyoxypropylene block polymers, (hydrolysed) collagen, (hydrolysed) elastin, (hydrolysed) keratin, collagen, gelatin, gum arabic and polyquaternium-X (1-10).

The polymeric material preferably used is cellulose.

To prepare a polymeric carrier material treated with a fluorescent whitening agent, the above-mentioned fluorescent whitening agents can be applied to an appropriate carrier. This can be carried out by mixing the carrier materials with the appropriate fluorescent whitening agent in a suitable solvent. When, for example, a solvent in which the fluorescent whitening agent is soluble but the polymeric carrier material is insoluble is used, the dissolved fluorescent whitening agent can be applied directly to the polymeric carrier material. The solvent can be removed from the resulting treated polymeric carrier material by suitable physical separating methods.

When a solvent, e.g. water, in which the fluorescent whitening agent and the polymeric carrier material are soluble, or - in the case of the carrier material - swellable, is used, the entire whitening agent/polymeric carrier material/solvent mixture can be incorporated into an appropriate cosmetic or pharmaceutical formulation. It is, however, also possible to remove the solvent from the mixture by suitable methods before the mixture is used further.

The polymeric carrier materials treated with a fluorescent whitening agent can also be prepared by chemical reaction of the polymeric carrier material with the appropriate fluorescent whitening agent.

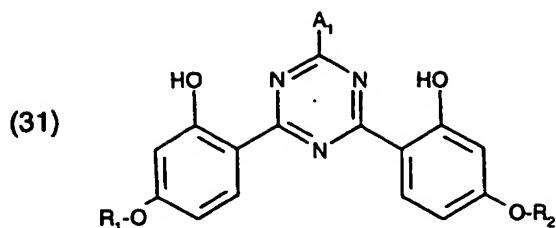
The polymeric carrier materials treated with a fluorescent whitening agent so obtained are suitable for lightening human skin. They simultaneously offer effective protection against UV radiation. A further advantage of such materials is that the actual active substance, that is the fluorescent whitening agent, does not come into direct contact with the skin.

For cosmetic and pharmaceutical use, the treated polymeric carrier materials can be incorporated into appropriate formulations.

The invention accordingly relates also to a cosmetic formulation that comprises a polymeric carrier material treated with a fluorescent whitening agent, as well as cosmetically tolerable carriers or adjuvants.

The cosmetic formulation may, in addition to containing the polymeric carrier material treated with a fluorescent whitening agent, also contain one or more further UV-protective substances from the following classes of substance:

1. p-aminobenzoic acid derivatives, e.g. 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
2. salicylic acid derivatives, e.g. salicylic acid 2-ethylhexyl ester;
3. benzophenone derivatives, e.g. 2-hydroxy-4-methoxybenzophenone and the 5-sulfonic acid derivative thereof;
4. dibenzoylmethane derivatives, e.g. 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione;
5. diphenyl acrylates, e.g. 2-ethylhexyl-2-cyano-3,3-diphenyl acrylate and 3-(benzofuranyl)-2-cyanoacrylate;
6. 3-imidazol-4-yl-acrylic acid and esters;
7. benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
8. polymeric UV absorbers, e.g. the benzylidene malonate derivatives described in EP-A-709 080;
9. cinnamic acid derivatives, e.g. the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester disclosed in US-A-5 601 811 and WO 97/00851;
10. camphor derivatives, e.g. 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethylene-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts;
11. trianilino-s-triazine derivatives, e.g. 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
12. 2-hydroxyphenyl-benzotriazole derivatives;
13. 2-phenylbenzimidazole-5-sulfonic acid and salts thereof;
14. menthyl-o-aminobenzoate;
15. TiO₂ (variously encapsulated), ZnO and mica;
16. hydroxyphenyltriazines, e.g. compounds of formula



wherein

R_1 and R_2 are each independently of the other C_3-C_{18} alkyl; C_2-C_{18} alkenyl; or a radical of formula $-CH_2-CH(-OH)-CH_2-O-T_1$; or

R_1 and R_2 are a radical of formula (31a) $\begin{array}{c} R_{13} \\ | \\ -R_{12}-[Si-R_{13}-O-Si-R_{15}-]^{p_1}-R_{14} \end{array}$;

R_{12} is a direct bond, a straight-chain or branched C_1-C_4 alkylene radical or a radical of formula $-C_{m_1}H_{2m_1}$ or $-C_{m_1}H_{2m_1}O-$;

R_{13} , R_{14} and R_{15} are each independently of the others C_1-C_{18} alkyl; C_1-C_{18} alkoxy or a

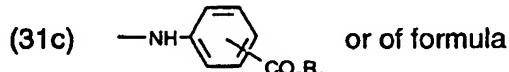
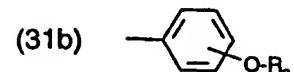
radical of formula $\begin{array}{c} R_{16} \\ | \\ -O-Si-R_{16}- \\ | \\ R_{16} \end{array}$;

R_{16} is C_1-C_5 alkyl;

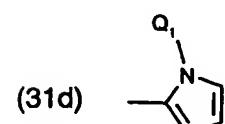
m_1 and m_3 are each independently of the other from 1 to 4;

p_1 is 0 or a number from 1 to 5;

A_1 is a radical of formula



or of formula



R_3 is hydrogen; C_1-C_{10} alkyl; $-(CH_2CHR_5-O)_{n_1}-R_4$; or a radical of formula

$-CH_2-CH(-OH)-CH_2-O-T_1$;

R_4 is hydrogen; M ; C_1 - C_5 alkyl; or a radical of formula $-(CH_2)_{m_2}-O-T_1$;

R_5 is hydrogen; or methyl;

T_1 is hydrogen; or C_1 - C_8 alkyl;

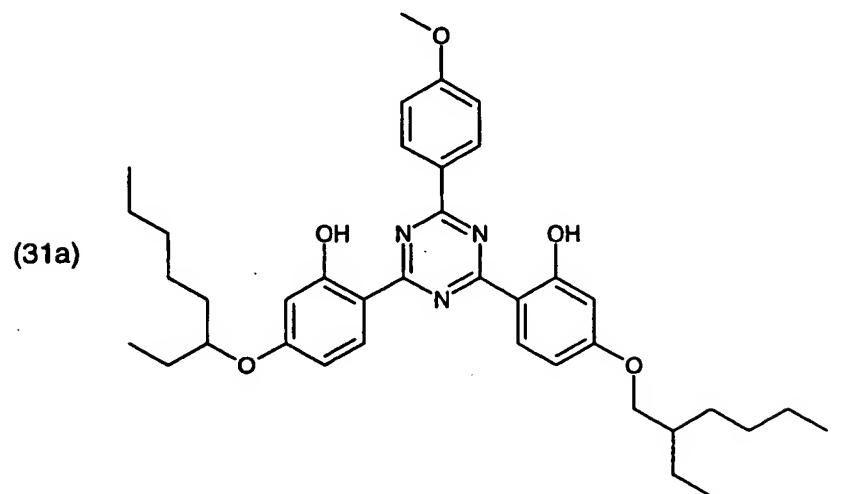
Q_1 is C_1 - C_{18} alkyl;

M is a metal cation;

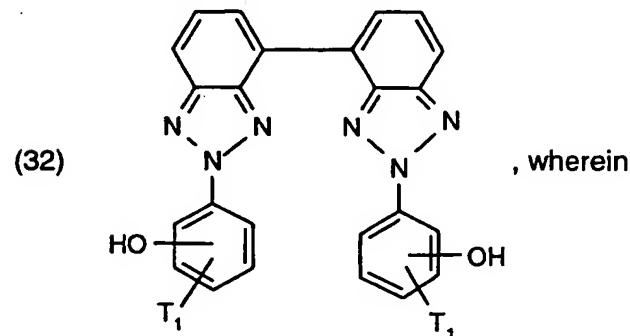
m_2 is from 1 to 4; and

n_1 is from 1 to 16;

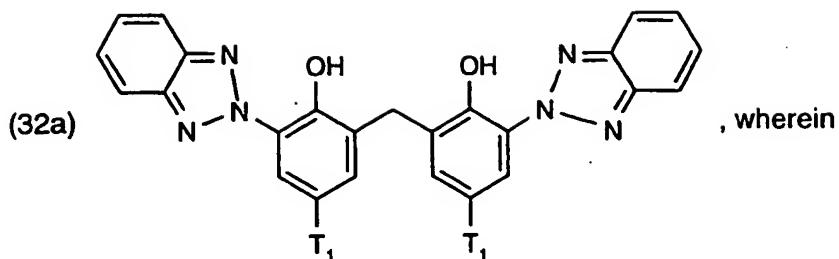
especially the triazine compound of formula



17. micronised organic UV absorbers, especially compounds of formula



T_1 is hydrogen; or C_1 - C_{12} alkyl; more especially benzotriazole compounds of formula



T_1 has the meanings given for formula (32) and is preferably methyl, tert-butyl or isoocetyl.

Also, the UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A. Shaath, Marcel Dekker, Inc., New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) can be used as additional UV-protective substances in the formulation according to the invention.

The cosmetic or pharmaceutical formulation according to the invention can furthermore also be used together with known antioxidants, e.g. vitamin E, carotenoids or flavonoids.

The cosmetic formulation according to the invention contains from 0.1 to 15 % by weight, preferably from 0.5 to 10 % by weight, based on the total weight of the composition, of a polymeric carrier material treated with a fluorescent whitening agent, as well as a cosmetically tolerable adjuvant.

The cosmetic or pharmaceutical formulation can be prepared by physically mixing the treated polymeric carrier material with the adjuvant using customary methods, e.g. by simply stirring together the individual components.

The cosmetic formulation according to the invention may be formulated as a water-in-oil or oil-in-water emulsion, as an oil-in-alcohol lotion, as a vesicular dispersion of an ionic or non-ionic amphiphilic lipid, as a gel, cream or lotion, a solid stick, powder, make-up, foam, paste, suspension or stick, or as an aerosol formulation.

In the case of a water-in-oil or oil-in-water emulsion, the cosmetically/pharmaceutically tolerable adjuvant contains preferably from 5 to 50 % of an oily phase, from 5 to 20 % of an emulsifier and from 30 to 90 % water. The oily phase may comprise any oil suitable for cosmetic/pharmaceutical formulations, e.g. one or more hydrocarbon oils, a wax, a natural oil, a silicone oil, a fatty acid ester or a fatty alcohol. Preferred mono- or poly-ols are ethanol, isopropanol, propylene glycol, hexylene glycol, glycerol and sorbitol.

Any conventionally used emulsifier can be used for the cosmetic or pharmaceutical formulation according to the invention, e.g. one or more ethoxylated esters of natural derivatives,

e.g. polyethoxylated esters of hydrogenated castor oil, or a silicone oil emulsifier, e.g. silicone polyol; a fatty acid soap which may or may not be ethoxylated; an ethoxylated fatty alcohol; a sorbitan ester which may or may not be ethoxylated; an ethoxylated fatty acid; or an ethoxylated glyceride.

The cosmetic or pharmaceutical formulation may also contain further components, e.g. emollients, emulsion stabilisers, skin humectants, thickeners, e.g. xanthan, moisture-retaining agents, e.g. glycerol, preservatives, perfumes and colourants.

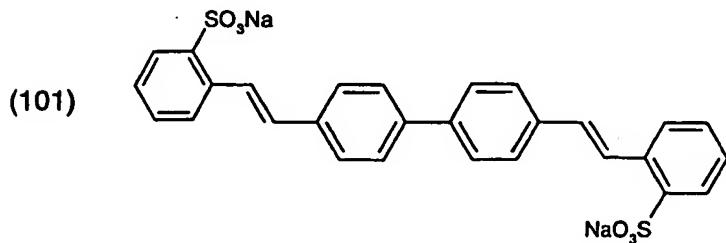
The carrier materials treated with a fluorescent whitening agent that can be used in accordance with the invention are also suitable for improving the appearance of cosmetic or pharmaceutical formulations. Frequently, the intrinsic colour especially of cosmetic formulations is an undesirable beige, or is even yellowish, as a result of the intrinsic colour of the components. The use of a polymeric carrier material treated with a fluorescent whitening agent according to the invention allows the degree of whiteness of such formulations to be increased. At the same time, the UV-absorbing properties of those carrier materials provides such products and their components with effective protection against the damaging effect of UV radiation.

The invention relates also to the use of the carrier materials treated with a fluorescent whitening agent for improving the degree of whiteness of cosmetic or pharmaceutical formulations.

The following Examples serve to illustrate the present invention.

Example 1: Fluorescent whitening agent immobilised on a starch derivative

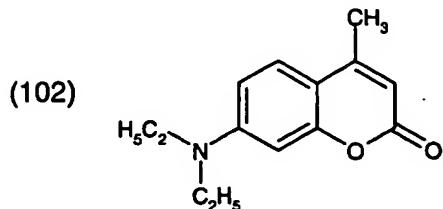
0.5 g of the fluorescent whitening agent of formula



is dissolved in 100 g of water. 30 g of aluminium starch-octenyl succinate are added thereto and the batch is stirred at room temperature for approximately 15 min.. The starch derivative is then filtered off and dried and is available for incorporation into formulations.

Example 2: Fluorescent whitening agent immobilised on an acrylate/tert-octylpropenamide copolymer

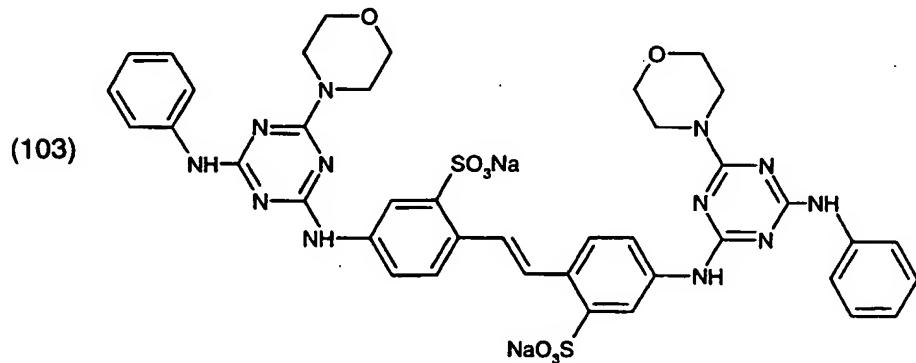
0.15 g of the compound of formula



is dissolved in 100 g of ethanol. Acrylate/tert-octylpropenamide copolymer (Dermacryl 79. National Starch) is added thereto and the batch is stirred at room temperature for approximately 15 min.. The polymer endowed with the fluorescent whitening agent is then precipitated by the addition of water, filtered off and dried.

Example 3: Fluorescent whitening agent immobilised on starch

0.3 g of the fluorescent whitening agent of formula



is dissolved in 100 g of water. Starch powder is added thereto and the batch is stirred at room temperature for approximately 15 min.. The starch endowed with the fluorescent whitening agent is then filtered off and dried.

Example 4: Preparation of a sun-protection cream

		<u>% w/w</u>
Phase (A)	octyl methoxycinnamate	7.50
	PEG 40 stearate	1.00
	glyceryl stearate SE	2.00
	cetyl alcohol	1.00
	C ₁₂ -C ₁₅ alkylbenzoates	5.00
	cyclomethicone	3.00
	phenyltrimethicone	1.00
	dimethicone copolyol	1.00
Phase (B)	deionised water	ad 100
	triethanolamine	4.00
	compound of formula (101)	1.00
	2-phenylbenzimidazole-5-sulfonic acid	4.00
	preservative	0.5 %
	carbomer 940 (2 % aqueous solution)	25.00
Phase (C)	propylene glycol	3.00
	aluminium-starch-octenyl succinate	3.00

With stirring at 80°C, phase (A) is introduced into phase B and the batch is homogenised.

Phase (C) (slurry) is added thereto at 40°C while stirring well and the batch is allowed to cool, with stirring.

On being applied thinly, the cream lightens the skin significantly.

Example 5: Preparation of an O/W sun-protection lotion

		<u>% w/w</u>
Phase (A)	polyglyceryl-3-methylglucose distearate	2.0
	decyloleate	5.7
	isopropyl palmitate	5.0
	caprylic/capric triglyceride	6.5
	compound of formula (31a)	2.0
	octylmethoxycinnamate	5.0
Phase (B)	glycerol	3.0
	Phenonip	0.5
	water	ad 100
Phase (C)	carbomer 141 + 0.002 g of compound of formula (101)	0.2
	isopropyl palmitate	0.8
Phase (D)	micronised UV absorber of formula (104) 	4.0
Phase (E)	NaOH (10 %)	as required

Phases (A) and (B) are separately heated to 80°C and combined without stirring. After the addition of (C), the batch is intensively homogenised. With gentle stirring, the batch is cooled to room temperature. The compound of formula (104) (D), adjusted to pH 5.5 using citric acid (20 % solution), is added in portions with careful stirring. For the purpose of thorough mixing, the batch is then stirred for a further 15 min.. Finally, the desired final pH value is set using (E).

On direct comparison with an emulsion without immobilised whitening agent, the so-prepared emulsion can clearly be distinguished as lighter ("whiter"), the slight yellowish colouration of the placebo formulation disappearing.

Example 6: Preparation of a W/O sun-protection emulsion

		<u>% w/w</u>
(A)	polyglyceryl-2-dipolyhydroxystearate	3
	glyceryl oleate	1
	caprylic/capric triglycerides	6
	octyl dodecanol	6
	Cetearyl isononanoate	5
	tocopheryl acetate	1
	fluorescent whitening agent of formula (102)	2
	cera alba	1.2
(B)	water	ad 100
	micronised UV absorber of formula (104)	10
	glycerol 86 %	5
	Phenonip	0.5

Phases (A) and (B) are separately heated to 75°C. With stirring, phase (B) is slowly added to phase (A) and the batch is slowly cooled down to 40°C. After brief intensive homogenisation, the batch is allowed to cool to room temperature with stirring.

Example 7: Preparation of a lotion

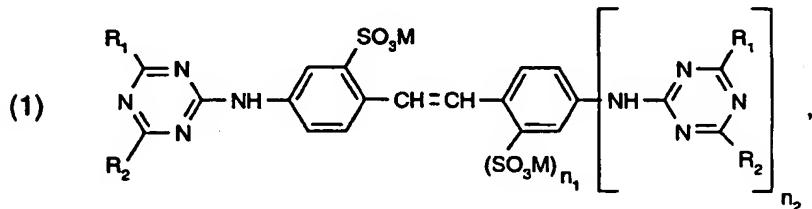
		<u>% w/w</u>
Phase (A)	cetyl alcohol	1.00 %
	glyceryl stearate	1.00
	ceteth 10	1.00
	C ₁₂ -C ₁₅ alkylbenzoate	5.00
	isopropyl palmitate	5.00
	dimethicone copolyol	1.00
	stearic acid	2.00
Phase (B)	deionised water	ad 100
	propylene glycol	3.00
	carbomer (Carbopol 940, 2 % in water)	8.00
	triethanolamine	0.70
	Phenonip	0.50
	fluorescent whitening agent of formula (103)	1.00

Phase (B) is heated to 80°C and maintained at that temperature for 20 min. with stirring.

Phase (A), likewise heated to 80°C, is added thereto with stirring and the batch is subsequently stirred for 10 min., cooled to 40°C and intensively homogenised. The batch is then allowed to cool to room temperature.

What is claimed is:

1. The use of a polymeric carrier material treated with a fluorescent whitening agent, for lightening human skin and for protecting human skin against UV radiation.
2. Use according to claim 1, wherein the polymeric carrier material comprises
 - (a) an oil-soluble or water-soluble fluorescent whitening agent;
 - (b) a polymeric compound and
 - (c) optionally, a solvent.
3. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula



wherein

R₁ is a radical of formula $-\text{NH}-\text{C}_6\text{H}_4-(\text{CO}_2\text{R}_3)_{x_1}$; $-\text{NH}-\text{C}_6\text{H}_4-\text{CO-R}_4$;

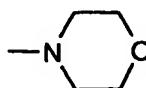
$-\text{NH}-\text{C}_6\text{H}_4-(\text{CN})_{x_2}$; or $-\text{NH}-\text{C}_6\text{H}_4-\text{SO}_2-\text{R}_5$; or is hal;

R₃ is M; or unsubstituted or substituted alkyl or unsubstituted or substituted aryl;

R₄ is hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or -NR₆R₇, wherein R₆ and R₇ are each independently of the other hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or R₆ and R₇ together with the nitrogen atom binding them form a heterocyclic radical, especially a morpholino or piperidino radical,

R₅ is hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted aryl; or a radical of formula (1a) $-(\text{CH}_2)_{x_2}-\text{O-SO}_3-\text{M}$;

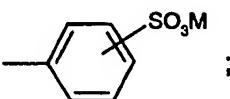
R_2 is hydrogen; unsubstituted or substituted alkyl or unsubstituted or substituted

aryl; or a radical of formula  , -OH; -NH₂; -N(CH₂CH₂OH)₂;

-N[CH₂CH(OH)CH₃]₂; -NH-R₃; -N(R₃)₂ or -OR₃; or

R_1 and R_2 are each independently of the other -OH, -Cl; -NH₂, -O-C₁-C₄alkyl, -O-aryl,
-NH-C₁-C₄alkyl, -N(C₁-C₄alkyl)₂, -N(C₁-C₄alkyl)(hydroxy-C₁-C₄alkyl),
-N(hydroxy-C₁-C₄alkyl)₂; -NH-aryl, morpholino; or S-C₁-C₄alkyl(aryl);

R_8 and R_9 are each independently of the other hydrogen, C₁-C₄alkyl, phenyl or a radical of

formula  ;

R_{10} is hydrogen, Cl or SO₃M;

R_{11} is -CN, -SO₃M, -S(C₁-C₄alkyl)₂ or S(aryl)₂;

R_{12} is hydrogen, -SO₃M, -O-C₁-C₄alkyl, -CN, -Cl, -COO-C₁-C₄alkyl or CON(C₁-C₄alkyl)₂;

R_{13} is hydrogen; -C₁-C₄alkyl, -Cl or -SO₃M;

R_{14} and R_{15} are each independently of the other hydrogen, C₁-C₄alkyl, -SO₃M, -Cl or
-O-C₁-C₄alkyl;

R_{16} is hydrogen or C₁-C₄alkyl;

R_{17} is hydrogen, C₁-C₄alkyl, -CN, -Cl, -COO-C₁-C₄alkyl, -CON(C₁-C₄alkyl)₂, aryl or -O-aryl;

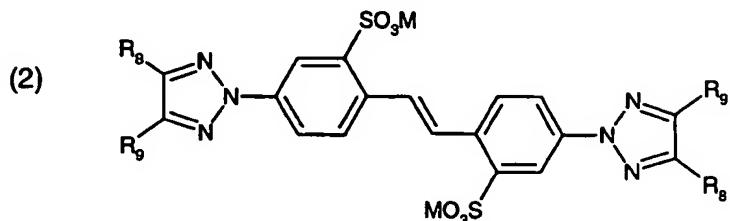
M is hydrogen, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C₁-C₄alkylammonium,
mono-, di- or tri-C₁-C₄hydroxyalkylammonium, or ammonium di- or tri-substituted by a
mixture of C₁-C₄alkyl and C₁-C₄hydroxyalkyl groups;

n_1 , n_2 and n_3 are each independently of the others 0 or 1;

x_1 is 1 or 2; and

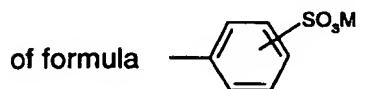
x_2 is from 1 to 3.

4. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula

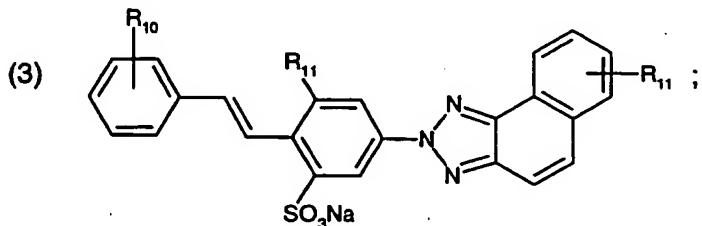


wherein

R₈ and R₉ are each independently of the other hydrogen; C₁-C₄alkyl; phenyl; or a radical



5. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula

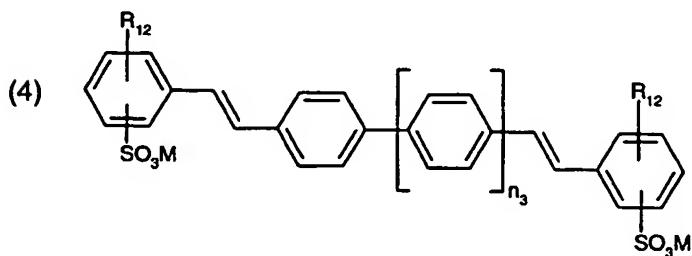


wherein

R₁₀ is hydrogen, Cl or SO₃M;

R₁₁ is -CN, -SO₃M, -S(C₁-C₄alkyl)₂ or S(aryl)₂.

6. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula



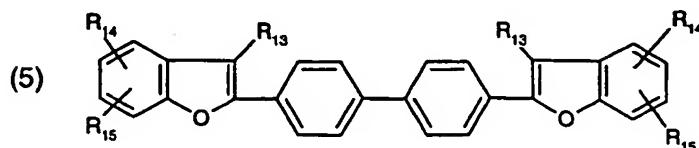
wherein

R_{12} is hydrogen, $-SO_3M$, $-O-C_1-C_4\text{alkyl}$, $-CN$, $-Cl$, $-COO-C_1-C_4\text{alkyl}$ or $CON(C_1-C_4\text{alkyl})_2$;

n_3 is 0; or 1; and

M has the meanings given in claim 3.

7. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula



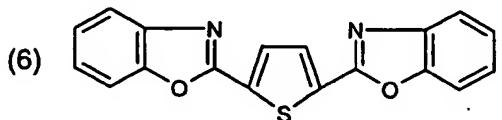
wherein

R_{13} is hydrogen; $-C_1-C_4\text{alkyl}$, $-Cl$ or $-SO_3M$;

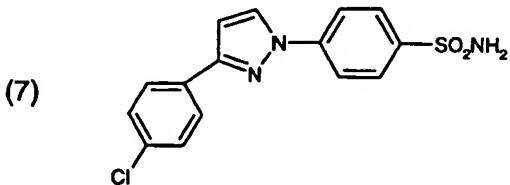
R_{14} and R_{15} are each independently of the other hydrogen, $C_1-C_4\text{alkyl}$, $-SO_3M$, $-Cl$ or $-O-C_1-C_4\text{alkyl}$; and

M has the meanings given in claim 3.

8. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula

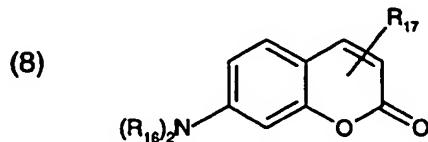


9. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula



- 27 -

10. Use according to either claim 1 or claim 2, which comprises using as fluorescent whitening agent a compound of formula



wherein

R₁₆ is hydrogen or C₁-C₄ alkyl;

R₁₇ is hydrogen, C₁-C₄ alkyl, -CN, -Cl, -COO-C₁-C₄ alkyl, -CON(C₁-C₄ alkyl)₂, aryl or -O-aryl.

11. Use according to any one of claims 1 to 10, which comprises using cellulose as polymeric carrier material.

12. A cosmetic formulation, comprising a polymeric carrier material treated with a fluorescent whitening agent, together with cosmetically tolerable carriers or adjuvants.

13. A pharmaceutical formulation, comprising a polymeric carrier material treated with a fluorescent whitening agent, together with pharmaceutically tolerable carriers or adjuvants.

14. A formulation according to either claim 12 or claim 13, which comprises in addition UV-protective substances.

15. The use of the polymeric carrier material treated with a fluorescent whitening agent for lightening and for protecting against UV radiation components of cosmetic and pharmaceutical formulations.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/12342

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 742 281 A (CIBA GEIGY AG) 13 November 1996 (1996-11-13) page 9, line 4-15; claims 1-9	1-15
A	WO 99 13822 A (SALVADOR DOROTHY YONG JUANICO ; MITSUMATSU ARATA (JP); PROCTER & GA) 25 March 1999 (1999-03-25) page 17 -page 18; claims 1-7; figures	1-15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
12 February 2001	20/02/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Beyss, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Jonal Application No

PCT/EP 00/12342

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0742281 A	13-11-1996	GB 2300644 A, B	JP 8302563 A	13-11-1996 19-11-1996
		US 5695687 A		09-12-1997
WO 9913822 A	25-03-1999	WO 9913848 A	AU 4486397 A	25-03-1999 05-04-1999